

# Relation between a Screened Polyelectrolyte and a Field Theory

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## Abstract

There exists a generic relationship between the thermodynamics of a continuous polymer with a generic self-interaction and the two-point function of an interacting field-theory. In addition, the  $(2N)$ -point function of the resulting field theory is similarly related to a system of  $N$  interacting polymers.

In the present paper, this relation is explored for the special case of a polyelectrolyte, characterized by a screened Coulomb pair potential. The corresponding field theory can be recast in a particularly simple form, corresponding to a quantum-mechanical particle, self-interacting via the emission and absorption of a massive scalar field.

This is particularly useful in a perturbative treatment: perturbative expansions for the polyelectrolyte can be simply derived from the loop expansion for the related field-theoretical two-point function, for which established computational methods exist.

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*Introduction* Relations between Euclidean field theories and random walks or polymers are well-known [1–6]. For a non-interacting continuous polymer, equivalent to a random walk, the relation to the propagator of a free field theory is trivial. For the case of a continuous polymer with a delta-function pair interaction, corresponding to a self-avoiding random walk, de Gennes has shown the relation to a  $\phi^4$  field theory (Landau-Ginsburg model) [2–5]. A similar relation has been exploited for an unscreened polyelectrolyte [7]. The focus of the present paper is to exploit the generic result for the special case of a screened polyelectrolyte, leading to a specific, very simple field-theory.

*The generic interacting polymer* A quite generic self-interacting discrete polymer with  $N$  monomers in  $D$ -dimensional space is described by the Hamiltonian

$$H(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{2} \sum_{i=1}^{N-1} (\mathbf{x}_{i+1} - \mathbf{x}_i)^2 + \sum_{i=1}^N \tilde{V}_1(\mathbf{x}_i) + \sum_{i=1}^N \sum_{j=i+1}^N \tilde{V}_2(\mathbf{x}_i, \mathbf{x}_j) + \sum_{i=1}^N \sum_{j=i+1}^N \sum_{k=j+1}^N \tilde{V}_3(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) + \dots,$$

where  $\mathbf{x}_i$  denotes the position in  $\mathcal{R}^D$  of the  $i$ th monomer. The first term represents a harmonic bonding force between nearest-neighbour monomers, while  $\tilde{V}_1(\mathbf{x})$  is a generic one-particle potential,  $\tilde{V}_2(\mathbf{x}, \mathbf{y})$  a ditto pair potential, etc. The interaction is the most general one that depends on positions only and is independent of monomer indices. Thermodynamic averages at temperature  $T$  are defined based on the Boltzmann distribution,  $P(\mathbf{x}_1, \dots, \mathbf{x}_N) \propto \exp(-H/T)$ .

For the Boltzmann exponent  $S \equiv H/T$ , we obtain in the continuum approximation, defined by replacing the discrete monomer index  $i$  by a continuous chain parameter  $\tau = Ti$ , such that  $\mathbf{x}_i \rightarrow \mathbf{x}(\tau) \equiv \mathbf{x}(Ti)$ , the following expression:

$$S[\mathbf{x}(\tau)] = \frac{1}{2} \int_0^\mu d\tau \dot{\mathbf{x}}^2 + \int_0^\mu d\tau V_1(\mathbf{x}(\tau)) + \frac{1}{2} \int_0^\mu d\tau \int_0^\mu d\tau' V_2(\mathbf{x}(\tau), \mathbf{x}(\tau')) + \frac{1}{6} \int_0^\mu d\tau \int_0^\mu d\tau' \int_0^\mu d\tau'' V_3(\mathbf{x}(\tau), \mathbf{x}(\tau'), \mathbf{x}(\tau'')) + \dots,$$

where square brackets  $[\ ]$  are used to indicate that  $S$  is a functional. The length of the polymer is represented by  $\mu = NT$ , while  $V_k \equiv \tilde{V}_k/T^{k+1}$ , for  $k = 1, 2, \dots$ . The dot in  $\dot{\mathbf{x}}$  stands for the derivative with respect to  $\tau$ . The continuum approximation is valid when the nearest-neighbour distances are small in comparison to the range of the interactions. The independence on monomer index is turned into a translation invariance with respect to the chain position  $\tau$ :  $V_n$  depends on  $(\tau, \tau', \dots)$  only via  $(\mathbf{x}(\tau), \mathbf{x}(\tau'), \dots)$ .

The continuum formulation will be the starting point for the analysis carried out in the rest of this letter, and  $S[\mathbf{x}(\tau)]$  will be referred to as the *action* of the system. To begin with, we will assume fixed B.C., with the endpoints of the chain locked at  $\mathbf{x}(0) = \mathbf{a}$ ,  $\mathbf{x}(\mu) = \mathbf{b}$ . The main object of interest is the *partition function*, which is given by the functional integral

$$Z(\mu, \mathbf{a}, \mathbf{b}) = \int_{\mathbf{x}(0)=\mathbf{a}}^{\mathbf{x}(\mu)=\mathbf{b}} d[\mathbf{x}(\tau)] \exp(-S[\mathbf{x}(\tau)]).$$

The proper partition function for free boundary conditions is obtained simply by integrating  $Z(\mu, \mathbf{a}, \mathbf{b})$  over the endpoints  $\mathbf{a}, \mathbf{b}$ .

*The relation to a field theory* The generic relation to a field-theory is has been described in the literature (see e.g. [6] and references therein). For the sake of completeness, we will here provide a derivation.

The translation-invariance of the interaction ensures that the interaction part  $S_{\text{int}}$  of the action be a functional only of the *particle density*,  $\rho(\mathbf{y}) = \int_0^\mu d\tau \delta(\mathbf{y} - \mathbf{x}(\tau))$ , in terms of which it is given by

$$\begin{aligned} & \int d\mathbf{x} \rho(\mathbf{x}) V_1(\mathbf{x}) + \frac{1}{2} \int d\mathbf{x} \rho(\mathbf{x}) \int d\mathbf{y} \rho(\mathbf{y}) V_2(\mathbf{x}, \mathbf{y}) + \\ & \frac{1}{6} \int d\mathbf{x} \rho(\mathbf{x}) \int d\mathbf{y} \rho(\mathbf{y}) \int d\mathbf{z} \rho(\mathbf{z}) V_3(\mathbf{x}, \mathbf{y}, \mathbf{z}) + \dots \end{aligned}$$

as a functional Taylor expansion. Next, we assume that the corresponding Boltzmann factor,  $\exp(-S_{\text{int}})$ , can be functionally Laplace transformed with respect to the (non-negative) particle density,

$$F[\xi(\mathbf{x})] = \int d[\rho(\mathbf{x})] \exp\left(-\int d\mathbf{x} \xi(\mathbf{x}) \rho(\mathbf{x}) - S_{\text{int}}[\rho]\right).$$

This is well-defined for any combination of arbitrary one-particle potentials and non-negative many-particle potentials. The functional Laplace transform can be inverted to yield, formally,

$$\exp(-S_{\text{int}}[\rho]) \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \exp\left(\int d\mathbf{x} \xi(\mathbf{x}) \rho(\mathbf{x})\right),$$

where each  $\xi(\mathbf{x})$  is to be integrated along a complex contour to the right of all singularities. We then obtain for the partition function

$$\begin{aligned} Z(\mu, \mathbf{a}, \mathbf{b}) & \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \times \\ & \int_{\mathbf{x}(0)=\mathbf{a}}^{\mathbf{x}(\mu)=\mathbf{b}} d[\mathbf{x}(\tau)] \exp\left(-\frac{1}{2} \int_0^\mu d\tau \dot{\mathbf{x}}^2 + \int_0^\mu d\tau \xi(\mathbf{x}(\tau))\right), \end{aligned}$$

and  $-\xi(\mathbf{x})$  appears as an effective one-particle potential for the polymer. Now the  $\mathbf{x}$  integral is recognized as the Euclidean quantum-mechanical path integral for the amplitude  $\langle \mathbf{a} | \exp(-\mu \hat{H}) | \mathbf{b} \rangle$  to go from  $\mathbf{a}$  to  $\mathbf{b}$  in imaginary time  $\mu$ , with the quantum-mechanical Hamiltonian

$$\hat{H} = -\frac{1}{2} \nabla^2 - \xi(\mathbf{x}) + \text{const..}$$

We thus have

$$Z(\mu, \mathbf{a}, \mathbf{b}) \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \langle \mathbf{a} | \exp(-\mu \hat{H}) | \mathbf{b} \rangle.$$

Now, we can make a Laplace transform in  $\mu$ ,

$$W(s, \mathbf{a}, \mathbf{b}) = \int_0^\infty d\mu \exp(-s\mu) Z(\mu, \mathbf{a}, \mathbf{b}),$$

yielding

$$W(s, \mathbf{a}, \mathbf{b}) \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \langle \mathbf{a} | (\hat{H} + s)^{-1} | \mathbf{b} \rangle.$$

The matrix-element can be written as a functional integral over a field  $\vec{\phi}(\mathbf{x})$  having  $n = 0$  components,

$$\begin{aligned} \langle \mathbf{a} | (\hat{H} + s)^{-1} | \mathbf{b} \rangle = \\ 2 \int d[\vec{\phi}(\mathbf{x})] \phi_1(\mathbf{a}) \phi_1(\mathbf{b}) \times \exp \left( - \int d\mathbf{x} \vec{\phi} (\hat{H} + s) \vec{\phi} \right), \end{aligned}$$

and we obtain

$$\begin{aligned} W(s, \mathbf{a}, \mathbf{b}) \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \int d[\vec{\phi}(\mathbf{x})] \phi_1(\mathbf{a}) \phi_1(\mathbf{b}) \times \\ \exp \left( - \int d\mathbf{x} \left\{ \frac{1}{2} (\nabla \vec{\phi})^2 + s \vec{\phi}^2 - \xi(\mathbf{x}) \vec{\phi}^2 \right\} \right). \end{aligned}$$

Now we can do the  $\xi$  integral to recover  $\exp(-S_{\text{int}}[\rho(\mathbf{x})])$ , but with a modified particle density,  $\rho(\mathbf{x}) \rightarrow \vec{\phi}(\mathbf{x})^2$ . Thus, we finally arrive at the following result:

$$W(s, \mathbf{a}, \mathbf{b}) \propto \int d[\vec{\phi}(\mathbf{x})] \phi_1(\mathbf{a}) \phi_1(\mathbf{b}) \exp \left( -\hat{S}[\phi(\mathbf{x})] \right).$$

The RHS defines the two-point function  $G(s, \mathbf{a}, \mathbf{b})$  of an interacting field theory, with an action  $\hat{S}$  given by

$$\begin{aligned} \hat{S}[\phi(\mathbf{x})] = \int d\mathbf{x} \left\{ \frac{1}{2} (\nabla \vec{\phi})^2 + s \vec{\phi}^2(\mathbf{x}) + V_1(\mathbf{x}) \vec{\phi}^2(\mathbf{x}) \right\} + \\ \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y} V_2(\mathbf{x}, \mathbf{y}) \vec{\phi}^2(\mathbf{x}) \vec{\phi}^2(\mathbf{y}) + \\ \frac{1}{6} \int d\mathbf{x} \int d\mathbf{y} \int d\mathbf{z} V_3(\mathbf{x}, \mathbf{y}, \mathbf{z}) \vec{\phi}^2(\mathbf{x}) \vec{\phi}^2(\mathbf{y}) \vec{\phi}^2(\mathbf{z}) + \dots \end{aligned}$$

This shows that the partition function for a generic interacting polymer, when Laplace transformed with respect to the chain-length  $\mu$ , yields the propagator of a zero-component field theory, with a bare mass determined by the corresponding conjugate variable  $s$ , and where the interaction appears in terms of a particle density given by the square of the field. Upon collecting the neglected constants of proportionality accumulated in the transformations, the exact relation is given by

$$2G(s, \mathbf{a}, \mathbf{b}) = \int_0^\infty d\mu \exp(-s\mu) \frac{Z(\mu, \mathbf{a}, \mathbf{b})}{\int d\mathbf{a} Z_0(\mu, \mathbf{a}, \mathbf{0})}$$

where  $Z_0$  denotes the partition function of a non-interacting polymer; the correctness can be verified by considering the case of no interactions, since the constants of proportionality involved do not depend on the interaction.

*Several polymers* Having established the relation between the partition function of an interacting polymer and the two-point function of a related field theory, one might wonder what is the relevance of the higher order moments in  $\vec{\phi}$ . It turns out (the proof is analogous to the one-polymer case) that the four-point function

$$\langle \phi_1(\mathbf{a})\phi_1(\mathbf{b})\phi_2(\mathbf{c})\phi_2(\mathbf{d}) \rangle$$

is proportional to the Laplace transform of the partition function for *two polymers*, one with its endpoints in  $\mathbf{a}$  and  $\mathbf{b}$ , the other in  $\mathbf{c}$  and  $\mathbf{d}$ , interacting both internally and with each other, and allowed to exchange monomers with each other: The parameter  $\mu$ , conjugate to  $s$ , merely fixes their *total length*. In addition, the moment

$$\langle \phi_1(\mathbf{a})\phi_1(\mathbf{b})\phi_1(\mathbf{c})\phi_1(\mathbf{d}) \rangle$$

corresponds to the sum of the three possible endpoint rearrangements of the two polymers. Similarly, the six-point functions are related to a system of three polymers, etc.

In contrast, a system of  $N$  polymers of *fixed lengths*  $\mu_i$  corresponds to, upon Laplace transforming each length individually, a field theory with distinct squared masses  $2s_i$  for  $N$  subsets (of zero components each) of the field components.

For dominantly repulsive interactions, the consideration of several polymers will of course make sense only in a finite volume (or finite polymer concentration).

*The screened polyelectrolyte* In the physically interesting case of a screened polyelectrolyte in three dimensions [8,9], having only a pair interaction given by a screened Coulomb potential,

$$V_2(\mathbf{x}, \mathbf{y}) = g \exp(-\kappa r)/4\pi r, \text{ with } r = |\mathbf{x} - \mathbf{y}|,$$

we have the resulting action

$$\begin{aligned} \hat{S}[\phi(\mathbf{x})] = & \int d\mathbf{x} \left\{ \frac{1}{2} (\nabla \vec{\phi})^2 + s \vec{\phi}^2(\mathbf{x}) \right\} + \\ & \frac{g}{2} \int d\mathbf{x} \int d\mathbf{y} \frac{\exp(-\kappa|\mathbf{x} - \mathbf{y}|)}{4\pi|\mathbf{x} - \mathbf{y}|} \vec{\phi}^2(\mathbf{x}) \vec{\phi}^2(\mathbf{y}). \end{aligned}$$

Noting that

$$\frac{\exp(-\kappa|\mathbf{x} - \mathbf{y}|)}{4\pi|\mathbf{x} - \mathbf{y}|} = (-\nabla^2 + \kappa^2)^{-1}(\mathbf{x}, \mathbf{y}),$$

we can make a further simplification by introducing an additional scalar field, the exchange of which mediates the interaction. This gives

$$\begin{aligned} W(s, \mathbf{a}, \mathbf{b}) \propto & \int d[\vec{\phi}(\mathbf{x})] \int d[\psi(\mathbf{x})] \phi_1(\mathbf{a})\phi_1(\mathbf{b}) \times \\ & \exp\left(-\tilde{S}[\phi(\mathbf{x}), \psi(\mathbf{x})]\right), \end{aligned}$$

with a *local* combined action  $\tilde{S}$  given by

$$\tilde{S}[\phi(\mathbf{x}), \psi(\mathbf{x})] = \int d\mathbf{x} \left\{ \frac{1}{2} (\nabla \vec{\phi})^2 + s \vec{\phi}^2 + \frac{1}{2} (\nabla \psi)^2 + \frac{1}{2} \kappa^2 \psi^2 + i\sqrt{g} \vec{\phi}^2 \psi \right\}.$$

The variable  $s$ , conjugate to the chain length  $\mu$ , appears only in the (bare)  $\vec{\phi}$  mass, while the inverse range  $\kappa$  of the interaction potential appears as the  $\psi$  mass; for the case of an unscreened potential, the  $\psi$ -field will be massless.

Now we can modify the boundary conditions; noting that the polymer is translationally and rotationally invariant, the partition function  $Z(\mu, \mathbf{a}, \mathbf{b})$  can depend only on  $R \equiv |\mathbf{a} - \mathbf{b}|$ . Integrating also over  $\mathbf{R}$  would yield the relevant partition function for the case of free boundary conditions. However, it adds no complication to include a factor  $\exp(i\mathbf{P} \cdot \mathbf{R})$  in the integral, yielding

$$\begin{aligned} W(s, \mathbf{P}) &= \int d\mathbf{R} \int_0^\infty d\mu \exp(-s\mu + i\mathbf{P} \cdot \mathbf{R}) Z(\mu, 0, \mathbf{R}) \\ &= \int_0^\infty d\mu \exp(-s\mu) \tilde{Z}(\mu, \mathbf{P}) \\ &\propto \int d\mathbf{R} \exp(i\mathbf{P} \cdot \mathbf{R}) G(0, \mathbf{R}) \equiv \tilde{G}(\mathbf{P}). \end{aligned}$$

This yields the two-point function in momentum space, at momentum  $\mathbf{P}$ , for the  $\vec{\phi}$  field. It contains all relevant information on the distribution of the end-to-end distance  $\mathbf{R}$  of the polymer. Thus, eg., the average end-to-end distance squared,  $\langle R^2 \rangle$ , can be obtained from

$$\frac{Z(\mu, \mathbf{P})}{Z(\mu, 0)} = 1 - \frac{P^2 \langle R^2 \rangle}{6} + \mathcal{O}(P^4).$$

*Relation in terms of perturbation theory* A perturbative (in the coupling  $g$ ) expansion for the polyelectrolyte is obtained by applying an inverse Laplace transform to the loop expansion for the resulting local field theory, the latter amounting to the well-known computation of Feynman graphs. In three dimensions, no ultraviolet divergences will appear, as can be seen from a simple dimensional analysis.

The Feynman rules for computing  $\tilde{G}(\mathbf{P})$  are simple: On a single  $\phi$  line add lines of emitted and re-absorbed  $\psi$  lines joining the first line in vertices. A  $\phi$  propagator carries a factor  $1/(q^2 + 2s)$  and a  $\psi$  propagator a factor  $1/(k^2 + \kappa^2)$ . For every vertex add a factor  $-2i\sqrt{g}$ . The external  $\phi$  momentum is given by  $\mathbf{P}$ , and momentum is conserved at every vertex. For every loop, add a momentum integral  $\int d^3p/(2\pi)^3$ . It is easy to see from dimensional counting, that in three dimensions the result will be ultra-violet finite for all graphs. Note that no  $\phi$ -loops are allowed (due to  $n = 0$ ); this can be interpreted as the  $\phi$ -field corresponding to a quantum-mechanical particle that is not second-quantized; thus, there can be no creation or annihilation of the corresponding particles.

Thus, to lowest order  $\tilde{G}(\mathbf{P})$  is given by the bare propagator

$$\tilde{G}^{(0)}(\mathbf{P}) = \frac{1}{P^2 + 2s}.$$

which is indeed half of the Laplace transform of  $\exp(-\mu P^2/2)$ , reflecting the distribution of  $\mathbf{R}$  for a free polymer being proportional to  $\exp(-\mathbf{R}^2/2\mu)$ . To first order in  $g$ , corresponding to one loop, there is only one graph contributing, displayed in Fig. 1, yielding

$$\begin{aligned}\tilde{G}^{(1)}(\mathbf{P}) &= \frac{-4g}{(P^2 + 2s)^2} \int \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{1}{(q^2 + \kappa^2)((\mathbf{P} - \mathbf{q})^2 + 2s)} \\ &= \frac{-4g}{(P^2 + 2s)^2} \frac{1}{4\pi P} \arctan\left(\frac{P}{\sqrt{2s + \kappa}}\right).\end{aligned}$$

To second order there are three distinct graphs, displayed in Fig. 2.

To compute the partition function  $Z$ , and related entities like  $\langle S_{\text{int}} \rangle$ , it is enough to consider  $\mathbf{P} = 0$ , while for  $\langle R^2 \rangle$ , the leading small  $P^2$  corrections must be taken into account. Work on perturbative calculations for the polyelectrolyte relying on the above analysis is in progress, and will be presented elsewhere [10].

In a similar way, any pair-potential that only depends on the relative position,  $V_2(\mathbf{x}, \mathbf{x}') = U(\mathbf{x} - \mathbf{x}')$ , can be perturbatively treated; provided the  $\psi$  propagator is replaced by the Fourier transform of the potential,  $\tilde{U}(\mathbf{q}) = \int d\mathbf{x} \exp(i\mathbf{q} \cdot \mathbf{x}) U(\mathbf{x})$ .

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# FIGURES

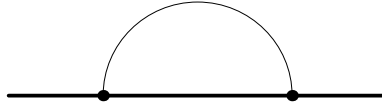


FIG. 1. The only graph contributing to first order in the perturbation expansion for  $\tilde{G}(\mathbf{P})$ .

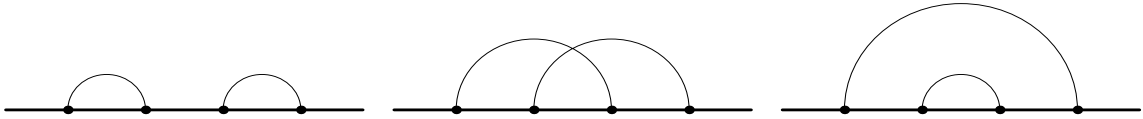


FIG. 2. The three graphs contributing to second order in the perturbation expansion for  $\tilde{G}(\mathbf{P})$ .